

The importance of nonlinear fluid response in joint density-functional theory studies of battery systems

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Abstract. Delivering the full benefits of first principles calculations to battery materials demands the development of accurate and computationally-efficient electronic structure methods that incorporate the effects of the electrolyte environment and electrode potential. Realistic electrochemical interfaces containing polar surfaces are beyond the regime of validity of existing continuum solvation theories developed for molecules, due to the presence of significantly stronger electric fields. We present an *ab initio* theory of the nonlinear dielectric and ionic response of solvent environments within the framework of joint density-functional theory, with precisely the same optimizable parameters as conventional polarizable continuum models. We demonstrate that the resulting nonlinear theory agrees with the standard linear models for organic molecules and metallic surfaces under typical operating conditions. However, we find that the saturation effects in the rotational response of polar solvent molecules, inherent to our nonlinear theory, are crucial for a qualitatively correct description of the ionic surfaces typical of the solid electrolyte interface.

1. Introduction

The development of better batteries is a critical step towards reducing energy reliance from oil to renewable energy resources. Experimental studies have historically made great progress in identifying promising battery materials [1], but a number of challenges remain. For instance, the solid electrolyte interfaces (SEI) [2] of the electrodes play a crucial role in the thermodynamics and kinetics of battery operation, but these surfaces are currently poorly understood. Experiments have yet to even conclusively determine the compositions of many of these surfaces [3]. Other important challenges include understanding reaction mechanisms at the surfaces of electrodes and identifying new electrode materials. These problems are well-suited for computational study, which can complement an experimental approach through inexpensive, rapid but accurate calculations.

However, electrochemical systems pose a unique challenge for theoretical studies: the processes of interest occur at an interface that requires simultaneous quantum-mechanical and statistical treatment. The electrode and reactants on its surface need to be described with a quantum-mechanical method in order to capture the level of detail required to predict chemical reactions. The liquid electrolyte plays an equally important role in determining the reaction pathways, and necessitates a statistical treatment due to the need to sample the configuration space of the liquid.

The most straightforward approach to a combined statistical and quantum mechanical calculation is *ab initio* molecular dynamics [4], which is expensive since adequate statistical sampling necessitates several thousands of steps at the electronic structure level of detail. This cost may be ameliorated by combining classical molecular dynamics with electronic structure only for relevant parts of the system, as in the Quantum Mechanics / Molecular Mechanics (QM/MM) methods [5]. However, statistical sampling issues and the need for coupling constant integration for estimating free energies complicate the analysis of the results of any molecular dynamics based method.

The complexity and computational cost due to statistical sampling can be avoided by working directly with equilibrium properties of the system. Joint density-functional theory (JDFT) [6] is an exact variational principle for the free energy of an electronic system in contact with a liquid, in terms of the densities of the two subsystems. This framework enables systematic approximations such as combining electronic density-functional theory for the system of interest with classical density-functional theory for the liquid environment.

Polarizable continuum models (PCM's) [7] are a class of highly efficient simplified theories where the effect of the fluid is captured by placing the electronic system in an appropriately chosen dielectric cavity, optionally with corrections for physical effects such as cavitation energies and dispersion interactions. However, the efficiency of these models comes at the cost of empiricism and a loss of key physical features of the fluid.

The empiricism of PCM approaches has been partially mitigated by constructing variants of the model [6, 8] that are highly simplified approximations within the framework of JDFT. So far, PCM approximations [6, 8, 9, 10] have replaced the fluid with a *linear* dielectric response which turns out to be adequate for the solvation of most molecules and some surfaces, such as those of metals. However, the highly polar surfaces typical of battery systems impose strong electric fields on solvents that invoke a highly nonlinear response; linear response approximations lead to qualitatively incorrect results as we demonstrate in Section 3.4.

In this paper, we present a systematic framework (Section 2.1) for developing PCM-like approximations within joint density-functional theory, and use it to construct a nonlinear polarizable continuum model (Sections 2.3 and 2.4) that is both inexpensive and sufficiently accurate to account for complex reactions, including those occurring on ionic surfaces. We show that the nonlinear dielectric model reproduces molecule solvation energies (Section 3.2), and with the inclusion of nonlinear ions, potentials of zero charge for metallic surfaces (Section 3.3) with accuracy similar to that of the linear model. Finally, we demonstrate that the inclusion of nonlinear dielectric saturation effects facilitates accurate predictions for ionic surfaces in solution (Section 3.4), making this model particularly suited for theoretical studies of battery materials.

2. Nonlinear polarizable continuum model

2.1. Joint density-functional theory framework for polarizable continuum models

The fundamental quantity of interest for *ab initio* studies of electrochemical and other solvated systems is the free energy of a quantum mechanical system in *equilibrium* with a liquid environment. Therefore, the most direct route to this quantity is a theory in terms of the equilibrium densities of the two subsystems. Joint density-functional theory (JDFT) [6] is based on an exact variational principle for this free energy in terms of these equilibrium densities, and provides a rigorous framework for the development of practical approximations.

The total free energy of such a system may be exactly partitioned as

$$A_{\text{JDFT}}[n, \{N_\alpha\}] = \underbrace{A_{\text{HK}}[n]}_{\text{electronic}} + \underbrace{\Phi_{\text{Lq}}[\{N_\alpha\}]}_{\text{liquid}} + \underbrace{\Delta A[n, \{N_\alpha\}]}_{\text{coupling}}, \quad (1)$$

where A_{HK} is the exact Hohenberg-Kohn electronic density functional [11], Φ_{Lq} is the exact free energy functional of the liquid [12], and the remainder, ΔA , is the free energy for the interaction of the two systems. Minimizing the above functional yields the ground state electron density $n(\mathbf{r})$ and the set of nuclear densities $\{N_\alpha(\mathbf{r})\}$ for the fluid.

In practice, each of the in-principle exact pieces of (1) needs to be approximated, and the power of the framework lies in the capability of independently selecting the level of approximation for each piece depending on the type of system, desired accuracy and available computational resources. The electronic system may be treated within the Kohn-Sham formalism [13] with any of the standard exchange-correlation functionals, or if necessary, with correlated quantum chemistry methods or quantum Monte Carlo methods as demonstrated in [14].

The liquid free energy may be treated within the rigid molecule classical density-functional theory formalism [15], with an approximation for the excess free energy of the liquid; reliable functionals for liquid water have been constructed from its equation of state [15, 16] and functionals for other liquids are available in the literature. (See [17] for a survey.) The interaction of the two subsystems, ΔA , may be treated using a density-only electronic density functional approach [18]. These approximations may be independently improved or simplified, as required for the system of interest.

Using a classical density-functional theory for the liquid within JDFT is a powerful tool for studying solvated electronic systems. However, the complexity of the theory can occasionally obscure an intuitive physical interpretation of the results. This

intuition may be better obtained from simpler and possibly less accurate versions of the theory that capture the bare minimum of physical effects required to describe the systems and properties of interest.

Polarizable continuum models (PCM) are highly simplified theories that account for liquid effects by embedding the electronic system in a dielectric cavity. The linear response approximation in PCM, however, is inadequate for the study of electrochemical systems that involve liquids in strong electric fields. Here, we develop a general framework for constructing PCM-like approximations within joint density-functional theory, which we use in the following sections to construct a nonlinear PCM with the same optimizable parameters as those of the linear model.

We start by dividing the liquid contributions to the free energy functional into physical effects assumed to be separable in polarizable continuum models, and rewrite the last two terms of (1) in the following form \ddagger

$$\begin{aligned} A_{\text{diel}} &\equiv \Phi_{\text{lq}} + \Delta A \\ &= A_\epsilon[s, \epsilon] + A_\kappa[s, \mu] + \int d\mathbf{r} \int d\mathbf{r}' \frac{\rho_{\text{lq}}(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} \left(\rho_{\text{el}}(\mathbf{r}) + \frac{\rho_{\text{lq}}(\mathbf{r})}{2} \right) + A_{\text{cav}}[s]. \end{aligned} \quad (2)$$

Dielectric response dominates the electrostatic interaction of a fluid consisting of neutral molecules alone, and the first term A_ϵ captures the corresponding internal energy. In addition to neutral solvent molecules, electrolytes typically include charged ions that contribute an additional monopole response. The optional term, A_κ , accounts for the internal energy of the ions if present in the solution. The densities of the molecules and ions of the solvent are modulated by the cavity shape function $s(\mathbf{r})$, which in turn is determined by the electron density $n(\mathbf{r})$.

The third term of (2) is the mean field electrostatic interaction of the liquid bound charge density ρ_{lq} with itself and the electronic system of total charge density ρ_{el} . Here, $\rho_{\text{lq}} \equiv \rho_\epsilon + \rho_\kappa$ includes dielectric and ionic contributions, while $\rho_{\text{el}} \equiv n + \rho_{\text{nuc}}$ includes contributions from the electrons and the nuclei (or pseudopotential cores) of the subsystem treated using electronic density-functional theory. The contributions from all remaining effects of the fluid, such as cavitation and dispersion, are gathered into the final term of (2), A_{cav} , and are assumed to depend only on the shape of the cavity $s(\mathbf{r})$. We detail specific approximations for each of these terms in the following subsections.

So far, the dielectric and ionic responses are still fully general, except for the mean-field assumption in their interaction with each other and the electronic system. In reality, these responses are nonlinear as well as nonlocal, while conventional polarizable continuum models [6, 7, 8, 9, 10] assume both linearity and locality. In this work, we retain the local response approximation, but develop a nonlinear theory for dielectric and ionic response in sections 2.3 and 2.4. We obtain a linear PCM comparable to [8] and [10] in Section 2.5 as the low-field limit of our general nonlinear theory.

2.2. Cavity shape function $s(\mathbf{r})$, and dependent energy A_{cav}

Polarizable continuum models replace the liquid with a dielectric cavity surrounding the electronic system. In variants of the model suitable for treating solid surfaces (which typically require a plane-wave basis), the dielectric constant is smoothly switched from the vacuum value of 1 to the bulk liquid value ϵ_b [6, 8, 9, 10]. The

\ddagger Here and throughout this paper, we use atomic units $4\pi\epsilon = e = \hbar = m_e = k_B = 1$.

spatial modulation of the dielectric constant may be written as $\epsilon(\mathbf{r}) = 1 + (\epsilon_b - 1)s(\mathbf{r})$, so that $s(\mathbf{r}) \in [0, 1]$ describes the shape of the cavity.

Further, these variants of PCM assume that the cavity shape $s(\mathbf{r}) = s(n(\mathbf{r}))$ is determined entirely by the local electron density. The exact functional form of $s(n)$ is not important as long as it switches smoothly between 0 at high electron densities and 1 at low electron densities, and rapidly approaches the extreme values away from the transition region. Following [6], for the rest of this work, we use

$$s(n) = \frac{1}{2} \operatorname{erfc} \frac{\log(n/n_c)}{\sigma\sqrt{2}} \quad (3)$$

where the parameter n_c sets the critical electron density around which the cavity smoothly ‘switches on’, and σ controls the width of that transition.

In the following subsections, we develop an *ab initio* theory for the nonlinear dielectric and ionic response of solvents, which we find to be the dominant effects at the charged or highly polar surfaces in electrochemical systems due to the strong electric fields. The cavity shape function, however, includes unknown parameters that are typically fit [7, 10] to reproduce the solvation energies of small organic molecules. These solvation energies are sensitive to other free energy contributions such as cavitation and dispersion, which although negligible in the electrochemical systems of interest, cannot be ignored during the determination of fit parameters.

These additional free energy contributions have complicated dependences on the shape of the cavity, for which several empirical approximations have been developed (see [7] for a review). Andreussi and coworkers [10] demonstrated that a simple empirical model expressing the sum of all these effects as an effective surface tension for the cavity works reasonably well for the solvation energies of small organic molecules. Since we need the additional effects only as auxiliary contributions during the fit to the molecular solvation data, we adopt their simplified model here by writing

$$A_{\text{cav}}[s] = \tau \underbrace{\int d\mathbf{r} |\nabla s|}_{S}, \quad (4)$$

where S is a surface area estimate for the cavity described by $s(\mathbf{r})$, and τ is an effective tension that is determined by the fit to solvation energies.

2.3. Nonlinear dielectric internal energy, A_ϵ

The dielectric response of liquids includes contributions from molecular polarizability as well as rotations of molecules with permanent dipole moments. The response of highly polar solvents such as water is dominated by rotations. With increasing field strength, the molecular dipoles increasingly align with the electric field, eventually saturating the rotational response. The polarizability response, which includes electronic polarizability and flexing modes of the molecules, typically becomes stronger at higher fields. It is therefore important to consider all these contributions even for solvents whose linear response is dominated by rotations.

The typical electric fields encountered in solvation can significantly saturate the rotational response of solvents, but are usually insufficient to access the nonlinear regime of the remaining contributions. We therefore split the internal energy of the dielectric A_ϵ into rotational A_{rot} and polarization A_{pol} parts, and construct a nonlinear theory for the rotational part alone.

Within the polarizable continuum ansatz, the liquid consists of molecules distributed with the bulk density N_{mol} modulated by the cavity shape function $s(\mathbf{r})$. The internal energy corresponding to linear polarization response with an effective molecular polarizability χ_{mol} is

$$A_{\text{pol}}[\mathbf{P}_{\text{pol}}] = \int d\mathbf{r} N_{\text{mol}} s(\mathbf{r}) \frac{1}{2} \chi_{\text{mol}} \mathbf{P}_{\text{pol}}^2(\mathbf{r}), \quad (5)$$

where $\mathbf{P}_{\text{pol}}(\mathbf{r})$ is the induced dipole moment per molecule. This dipole moment contributes a bound charge, $\rho_{\text{pol}}(\mathbf{r}) = -\nabla \cdot (N_{\text{mol}} s(\mathbf{r}) \mathbf{P}_{\text{pol}}(\mathbf{r}))$.

Physically, the nonlinearity of the rotational response arises from a competition between the rotational entropy of the molecules and their interaction with the self-consistent electric field. We therefore begin with the exact rotational entropy for an ideal gas of dipoles with the cavity-prescribed density $N_{\text{mol}} s(\mathbf{r})$ at temperature T , then approximate rotational correlations, and write

$$A_{\text{rot}}[p_e, l] = \int d\mathbf{r} T N_{\text{mol}} s(\mathbf{r}) \left[\int \frac{d\mathbf{e}}{4\pi} p_e \log p_e - l(\mathbf{r}) \left(\int \frac{d\mathbf{e}}{4\pi} p_e - 1 \right) - \frac{\alpha \mathbf{P}_{\text{rot}}^2(\mathbf{r})}{2} \right]. \quad (6)$$

Here, $p_e(\mathbf{r})$ is the probability that a molecule at location \mathbf{r} has its dipole oriented along unit vector \mathbf{e} , and the second term of (6) constrains the normalization of $p_e(\mathbf{r})$ with Lagrange multiplier field $l(\mathbf{r})$.

The final term of (6) captures the correlations in dipole rotations within a ‘local polarization density approximation (LPDA)’. We choose the simplest possible form for this correction, quadratic in the local dimensionless polarization $\mathbf{P}_{\text{rot}}(\mathbf{r}) = \int \frac{d\mathbf{e}}{4\pi} p_e(\mathbf{r}) \mathbf{e}$, and constrain the prefactor α to reproduce the bulk linear dielectric constant ϵ_b . Finally, the rotational response contributes a bound charge $\rho_{\text{rot}}(\mathbf{r}) = -\nabla \cdot (p_{\text{mol}} N_{\text{mol}} s(\mathbf{r}) \mathbf{P}_{\text{rot}}(\mathbf{r}))$ within the local response approximation, where p_{mol} is the permanent molecular dipole moment.

The Euler-Lagrange equation for minimizing the total free energy with respect to p_e implies that, at equilibrium, the orientation distribution must be of the form $p_e = \exp(\boldsymbol{\varepsilon} \cdot \mathbf{e})$ for some vector field $\boldsymbol{\varepsilon}(\mathbf{r})$. Using the remaining Euler-Lagrange equations to eliminate $\mathbf{P}_{\text{pol}}(\mathbf{r})$ and $l(\mathbf{r})$ in favor of $\boldsymbol{\varepsilon}(\mathbf{r})$, the sum of (5) and (6) simplifies to

$$A_\epsilon[\boldsymbol{\varepsilon}(\mathbf{r})] = \int d\mathbf{r} T N_{\text{mol}} s(\mathbf{r}) \left[\boldsymbol{\varepsilon}^2 \left(f(\boldsymbol{\varepsilon}) - \frac{\alpha}{2} f^2(\boldsymbol{\varepsilon}) + \frac{X}{2} (1 - \alpha f(\boldsymbol{\varepsilon}))^2 \right) - \log \frac{\sinh \boldsymbol{\varepsilon}}{\boldsymbol{\varepsilon}} \right], \quad (7)$$

with corresponding dielectric bound charge

$$\rho_\epsilon(\mathbf{r}) = -\nabla \cdot [p_{\text{mol}} N_{\text{mol}} s(\mathbf{r}) \boldsymbol{\varepsilon} (f(\boldsymbol{\varepsilon}) + X(1 - \alpha f(\boldsymbol{\varepsilon})))]. \quad (8)$$

Here, $f(\boldsymbol{\varepsilon}) = (\boldsymbol{\varepsilon} \coth \boldsymbol{\varepsilon} - 1)/\boldsymbol{\varepsilon}^2$ is the effective dimensionless rotational susceptibility defined by $\mathbf{P}_{\text{rot}} = f(\boldsymbol{\varepsilon}) \boldsymbol{\varepsilon}$, and $X \equiv \chi_{\text{mol}} T / p_{\text{mol}}^2$ is its counterpart for the linear polarization response.

The resulting theory for the dielectric has four solvent-dependent parameters (N_{mol} , p_{mol} , X and α), of which the bulk molecular density, N_{mol} , is directly measurable. The effective molecule dipole moment in the liquid, p_{mol} , differs from the gas-phase value, and in principle, can be determined from measurements of the lowest order nonlinear response coefficient [19]. However, such measurements are difficult and not readily available for most solvents. Instead, we compute p_{mol} as the self-consistent dipole moment of a single solvent molecule in a solvated *ab initio* calculation employing a nonlinear polarizable continuum description of the same solvent. The resulting dipole moment for the solvents used in this work are listed in table 3. Note that p_{mol} is larger

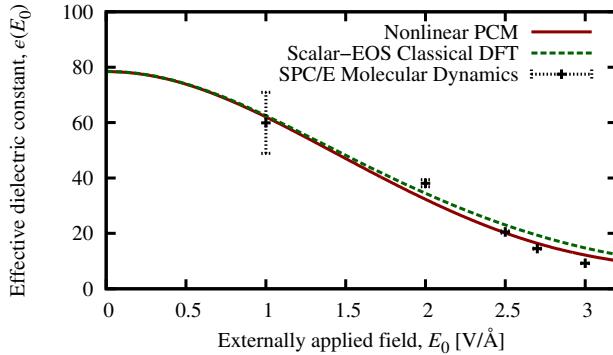


Figure 1. Comparison of the effective dielectric constant of water as a function of uniform externally applied field E_0 for the nonlinear PCM model (7) compared to SPC/E molecular dynamics results [21] and classical density functional predictions [15]. The effective dielectric constant is defined by $\epsilon = E_0/E$, where $E = E_0 - 4\pi P$ is the net electric field including the screening due to the dielectric polarization density P . Within this theory, this response is determined entirely by bulk liquid properties ϵ_b , ϵ_∞ and N_{mol} , along with the molecule dipole moment p_{mol} obtained from a self-consistent ab initio calculation solvated with the present model.

than the gas phase dipole moment for all these solvents because charged centers in the molecule are surrounded by bound charges of the opposite sign which favor an increase in the polarization, as shown for water in figure 2. We also find that for water, $p_{\text{mol}} = 0.94ea_0$ gratifyingly agrees with the SPC/E molecular dynamics model value of $0.92ea_0$ [20], in contrast to the gas phase value of $0.73ea_0$.

The remaining solvent-dependent parameters, the correlation factor for rotations α and the effective dimensionless polarizability X , are constrained to reproduce the bulk static and high frequency dielectric constants, ϵ_b and ϵ_∞ respectively. Using the bulk linear response of the above functional, we can analytically show that

$$X = \frac{T(\epsilon_\infty - 1)}{4\pi N_{\text{mol}} p_{\text{mol}}^2} \quad \text{and} \quad \alpha = 3 - \frac{4\pi N_{\text{mol}} p_{\text{mol}}^2}{T(\epsilon_b - \epsilon_\infty)}, \quad (9)$$

since the rotational response freezes out and does not contribute to ϵ_∞ . In principle, ϵ_∞ should be the dielectric constant at infrared frequencies between the rotational and vibrational resonances, but in the absence of experimental data in that frequency regime, we use the readily measurable optical dielectric constant, which is the square of the refractive index.

We have therefore produced a density-functional theory for the nonlinear dielectric response of an arbitrary solvent constrained entirely by measurable macroscopic properties. The response at field strengths relevant for solvation is not accessible experimentally, but it has been estimated using molecular dynamics. Figure 1 demonstrates that the bulk nonlinear dielectric response of the present theory is in excellent agreement with molecular dynamics results for water[21] using the SPC/E pair potential model [20]. The present theory, which uses LPDA for rotational correlations, produces essentially the same nonlinear response to uniform electric fields as classical density functional theories with the scaled mean-field electrostatics approximation [22]. The minor differences between the present theory and the classical density functional results [15] shown in Figure 1 are due to electrostriction; the latter

theory accounts for changes in the equilibrium fluid density in the presence of a strong uniform electric field.

2.4. Nonlinear ionic system internal energy, A_κ

The previous section derived the dielectric response of liquids from the dipolar rotational and polarization response of liquid molecules to the local electric field. Ionic species in the liquid introduce Debye screening by contributing an additional monopolar response, which changes the local ionic density in response to the local electric potential. A simple description of this response at the linearized Poisson-Boltzmann level suffices for many electrochemical systems [8]. For the electrode-electrolyte interface, this level of theory corresponds roughly to the Gouy-Chapman-Stern model, but misses the nonlinear capacitance effects due to ion adsorption. Here, we explore whether a full Poisson-Boltzmann treatment within the polarizable continuum model ansatz captures these additional details.

To represent the internal free energy of an ionic system comprising several species of charge Z_i and bulk concentrations N_i each, we employ the exact expression for the ideal gas of point particle ions, approximating finite-size effects with a local density approximation, and write

$$A_\kappa[\{\eta_i(\mathbf{r})\}] = T \sum_i \int d\mathbf{r} N_i s(\mathbf{r}) \left[\underbrace{(\eta_i(\log \eta_i - 1) + 1)}_{\text{Ideal gas}} + \underbrace{\frac{(x(\mathbf{r}) - x_0)^2}{x_0(1 - x_0)^2(1 - x(\mathbf{r}))^2}}_{\text{Hard sphere}} \right]. \quad (10)$$

The density of each ionic species is $N_i s(\mathbf{r}) \eta_i(\mathbf{r})$, represented in terms of the enhancement $\eta_i(\mathbf{r})$ relative to the cavity prescription of $N_i s(\mathbf{r})$. The charge-weighted sum of these densities contribute a net ionic bound charge $\rho_\kappa = \sum_i Z_i N_i s(\mathbf{r}) \eta_i(\mathbf{r})$.

The first ideal gas term in (10) along with the mean-field electrostatic interaction in the third term of (2) correspond to the Poisson-Boltzmann theory. That theory, however, does not limit the density of the ions in solution and presents an unphysical instability associated with infinite build-up of ions at regions of strong external potential. We resolve this instability by enforcing a packing limit on the ions via the second term of (10). This term captures local hard sphere correlations in terms of the packing fraction $x(\mathbf{r}) = \sum_i V_i N_i \eta_i(\mathbf{r})$, where $V_i = 4\pi R_i^3/3$ is the volume per ion for each species (with ionic radius R_i). The functional form of this term is constrained to reproduce $x(\mathbf{r}) \rightarrow x_0 \equiv \sum_i V_i N_i$ in the bulk and to match the divergence in the equation of state of the hard sphere fluid [23] as $x \rightarrow 1$.

2.5. Linear limit

The free energy functional (2) with dielectric free energy A_ϵ given by (7) and optional ionic free energy A_κ given by (10) constitutes our nonlinear polarizable continuum model. Here, we show that the conventional linear polarizable continuum model is a limit of this more general theory.

The rotational response from the dielectric is approximately linear when the energy scale of the molecular dipoles interacting with the field is much lower than the temperature ($p_{\text{mol}} |\nabla \phi| \ll T$), where $\phi(\mathbf{r})$ is the total electrostatic potential. Similarly, the ionic response is approximately linear when $Z|\phi| \ll T$. Using the Euler-Lagrange equations to eliminate $\boldsymbol{\epsilon}(\mathbf{r})$ and $\mu(\mathbf{r})$ in favor of $\nabla \phi(\mathbf{r})$ and $\phi(\mathbf{r})$

respectively, expanding the free energy to quadratic order, and simplifying using (9) and the definition $\kappa^2 \equiv 8\pi N_{\text{ion}} Z^2 / T$, we find

$$A_\epsilon + A_\kappa = \frac{1}{4\pi} \int d\mathbf{r} s(\mathbf{r}) \left[(\epsilon_b - 1) \frac{|\nabla\phi|^2}{2} + \kappa^2 \frac{\phi^2}{2} \right], \quad (11)$$

with the corresponding total bound charge at linear order

$$\rho_{\text{lq}}(\mathbf{r}) = \frac{1}{4\pi} [(\epsilon_b - 1) \nabla \cdot (s(\mathbf{r}) \nabla \phi) - \kappa^2 s(\mathbf{r}) \phi]. \quad (12)$$

The Euler-Lagrange equation for this simplified linear-response functional in terms of the single independent variable, ϕ , can be rearranged into the familiar modified Poisson equation (or Helmholtz equation for non-zero κ)

$$\nabla^2 \phi(\mathbf{r}) + (\epsilon_b - 1) \nabla \cdot (s(n(\mathbf{r})) \nabla \phi(\mathbf{r})) - \kappa^2 s(n(\mathbf{r})) \phi(\mathbf{r}) = -4\pi \rho_{\text{el}}(\mathbf{r}). \quad (13)$$

Finally, substituting the solution of (13) in the fluid free energy functional (2) with the dielectric and ionic energies given by (11), yields an equilibrium value for A_{diel} in the linear limit

$$A_{\text{diel}}^{(\text{linear})} = A_{\text{cav}} + \frac{1}{2} \int d\mathbf{r} \rho_{\text{el}}(\mathbf{r}) \left(\phi(\mathbf{r}) - \int d\mathbf{r}' \frac{\rho_{\text{el}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right). \quad (14)$$

Thus, the free energy functional approach to polarizable continuum models reduces, in the linear limit, to the standard approach [8, 10] of replacing the vacuum Poisson equation with one modified by the fluid.

2.6. Periodic systems and net charge

An important class of applications of the nonlinear polarizable continuum model, and joint density-functional theory in general, is the study of electrochemical systems. These systems pose an interesting challenge as they often involve charged metal or doped semiconducting surfaces. The periodic boundary conditions necessary to accurately describe the delocalized electronic states of such systems complicate the addition of charge, since the energy per unit cell of a periodic system with net charge per unit cell is divergent.

Including a counter electrode [24] to keep the simulation cell neutral avoids this problem, but leads to wasted computational effort on irrelevant portions of the system and complicates the separation of physics at the two electrodes. Introducing Debye screening due to ions in the electrolyte neutralizes the unit cell with fluid bound charge and naturally captures the physics of the electrochemical double layer [8]. More importantly, unlike the Poisson equation obtained without ionic screening, the Helmholtz equation for the electrostatic potential with screening (13) has a well-defined constant offset ('zero' of potential) in periodic boundary conditions. The resulting Kohn-Sham eigenvalues, and hence the electron chemical potential, correspond to a zero reference deep within the fluid, and this enables calibration of the electron chemical potential in DFT against electrochemical reference electrodes. (See [8] for details.)

The electrostatic potential in the nonlinear polarizable continuum model is not obtained from a Helmholtz equation, and the bound charge in the ionic system does not neutralize a net charge in the electronic system at an arbitrary value of the independent variable $\mu(\mathbf{r})$. Here, we present the modifications required to correctly handle periodic systems within the nonlinear ionic screening model.

The mean-field Coulomb energy per unit cell of volume Ω for the entire system with total charge density $\rho_{\text{tot}} = \rho_{\text{el}} + \rho_{\text{lq}}$ can be written in the plane-wave basis as $U = \frac{1}{2\Omega} \sum_{\mathbf{G}} \tilde{K}_{\mathbf{G}} |\tilde{\rho}_{\text{tot}}(\mathbf{G})|^2$. Here, $\tilde{\rho}_{\text{tot}}(\mathbf{G}) = \int_{\Omega} d\mathbf{r} \rho_{\text{tot}}(\mathbf{r}) \exp(-i\mathbf{G} \cdot \mathbf{r})$ for reciprocal lattice vectors \mathbf{G} , and $\tilde{K}_{\mathbf{G}} = 4\pi/G^2$ is the plane-wave basis Coulomb kernel. The divergent contribution at $G = 0$ vanishes for neutral unit cells with $Q_{\text{tot}} \equiv \tilde{\rho}_{\text{tot}}(0) = 0$.

The G^{-2} divergence results from the long-range $1/r$ tail of the Coulomb kernel. We can analyze the effect of the divergence by making the Coulomb kernel short-ranged on a length scale L much larger than the unit cell, and set $L \rightarrow \infty$ at the end. The exact form of the regularization is not important; picking the Gaussian-screened potential $\text{erfc}(r/L)/r$ results in the regularized Coulomb energy

$$U_L = \sum_{\mathbf{G} \neq 0} \frac{2\pi}{G^2 \Omega} |\tilde{\rho}_{\text{tot}}(\mathbf{G})|^2 + \frac{\pi L^2}{2\Omega} Q_{\text{tot}}^2. \quad (15)$$

Note that the first term employs the standard Coulomb kernel in the plane-wave basis which drops the $G = 0$ term by invoking a neutralizing background, and the second term contains the divergent part depending only on the total charge per unit cell.

At finite large L , the second term of U_L penalizes $Q_{\text{tot}} \neq 0$ and favors equilibrium configurations with small Q_{tot} . The Euler-Lagrange equation for the net charge Q_{tot} is $\lambda \equiv \partial A / \partial Q_{\text{tot}} = -\pi L^2 Q_{\text{tot}} / \Omega$, where A is the total free energy excluding the divergent second term of (15). Note that $\partial A / \partial Q_{\text{tot}}$ is finite for systems capable of adjusting their total charge, such as fluids with ionic screening, so that as $L \rightarrow \infty$, $Q_{\text{tot}} \rightarrow 0$ in such a manner that $\lambda \propto Q_{\text{tot}} L^2$ remains finite. The absolute potential is also well defined in this situation with a $G = 0$ contribution of $\partial U_L / \partial Q_{\text{tot}} = \pi L^2 Q_{\text{tot}} / \Omega = -\lambda$. Finally, note that

$$U_{\infty} = \sum_{\mathbf{G} \neq 0} \frac{2\pi}{G^2 \Omega} |\tilde{\rho}_{\text{tot}}(\mathbf{G})|^2 - \lambda Q_{\text{tot}} \quad (16)$$

results in the same Euler-Lagrange equation and equilibrium free energy as (15) in the $L \rightarrow \infty$ limit, and therefore the divergent term in the Coulomb energy reduces to a charge-neutrality constraint imposed by Lagrange multiplier λ .

We incorporate this Lagrange multiplier constraint into the ionic free energy in plane-wave calculations, and retain the standard plane-wave Coulomb kernel with $G = 0$ projected out for all electrostatic interactions. The constraint can be solved analytically for local nonlinear ions (section 2.4) in the commonly encountered case of a ‘Z:Z’ electrolyte consisting of two species of charge $+Z$ and $-Z$ (labeled with indices $i = +, -$) with bulk concentrations N_{ion} each. In this situation, we can show that substituting $\eta_{\pm}(\mathbf{r}) = \exp(\pm(\mu_0 + \mu_{\pm}(\mathbf{r})))$, where $\mu_0 \equiv -Z\lambda/T$ is obtained by solving the neutrality constraint, reduces the constrained minimization over $\eta_{\pm}(\mathbf{r})$ to an unconstrained minimization over $\mu_{\pm}(\mathbf{r})$. In particular, the neutrality constraint $Q_+ e^{\mu_0} + Q_- e^{-\mu_0} + Q_{\text{el}} = 0$ yields

$$\mu_0 = \log \frac{\sqrt{Q_{\text{el}}^2 - 4Q_+ Q_-} - Q_{\text{el}}}{2Q_+}, \quad (17)$$

where $Q_{\pm} \equiv \pm N_{\text{ion}} Z \int d\mathbf{r} s(\mathbf{r}) e^{\pm \mu(\mathbf{r})}$ and $Q_{\text{el}} \equiv \int d\mathbf{r} \rho_{\text{el}}(\mathbf{r})$ is the total charge of the electronic system. In this case, and for other joint density-functional theories which include ionic screening, the constraint contribution to $\delta A_{\text{diel}} / \delta \rho_{\text{el}}(\mathbf{r})$ in the electron potential establishes the absolute reference for the Kohn-Sham eigenvalues and the electron chemical potential required for *ab initio* electrochemistry [8].

2.7. Implementation

The nonlinear polarizable continuum model presented here and its linear counterpart have been implemented in the open source plane-wave electronic structure software JDFTx [25], designed for joint density-functional theory. The electronic density-functional theory segment of this software is based on conjugate gradients minimization [26] of an analytically continued total energy functional [27], expressed in the DFT++ algebraic formulation [28]. The fluid segment of JDFTx also employs the plane-wave basis and is discretized in the algebraic formulation for classical density-functional theories [15].

The valence electron density $n(\mathbf{r})$ from standard pseudopotentials need to be augmented with a core electron density to prevent overlap of the fluid with the pseudopotential cores [8]. Hence, we compute the shape function using (3) with $n_{\text{cav}}(\mathbf{r}) = n(\mathbf{r}) + n_{\text{core}}(\mathbf{r})$, where n_{core} is the partial core density used for nonlinear core corrections [29].

The electrostatic interactions with the fluid involve the total charge density (both electronic and nuclear) of the material described in the electronic structure portion of the calculation, $\rho_{\text{el}}(\mathbf{r}) = n(\mathbf{r}) + \rho_{\text{nuc}}(\mathbf{r})$. Here, the nuclear charge density, $\rho_{\text{nuc}}(\mathbf{r}) = -\sum_i Z_i e^{-(\mathbf{r}-\mathbf{r}_i)^2/(2w^2)}/(2\pi w)^{3/2}$ § is widened by a Gaussian resolvable on the charge density grid. The widened nuclear density is used only in the interaction with the fluid; the internal energies of the electronic system employ point nuclei in all terms. This width does not affect the interaction energy since the fluid and nuclear charge densities do not overlap, and the nuclear charge is spherically symmetric. However, it shifts the potential relative to the zero-width case, which we compensate exactly by adding the correction $-2\pi w^2 \sum_i Z_i/\Omega$ to the electron potential, where Ω is the unit cell volume.

Finally, regarding algorithms, the linear polarizable continuum models are minimized by solving the Helmholtz (or Poisson) equation (13) at every electronic iteration. Appropriate preconditioners for the involved linear conjugate gradients solver have been developed previously [8]. The free energy of the nonlinear polarizable continuum model is minimized using the Gummel iteration [30], where the electronic system and the fluid are alternately minimized while holding the state of the other one frozen. This method is guaranteed to be globally convergent due to the variational principle, and typically converges adequately in 5-10 alternations for most systems studied. The fluid free energy A_{diel} is minimized with the scalar field $\mu(\mathbf{r})$ and vector field $\boldsymbol{\varepsilon}(\mathbf{r})$ as independent variables; the diagonal preconditioner in reciprocal space ||

$$K_\mu(\mathbf{G}) = \left[\frac{Z(1-\alpha/3)}{p_{\text{mol}}} \right]^2 \frac{G^2}{(G^2 + \kappa^2/\epsilon_b)^2} \quad (18)$$

for the μ channel with the identity preconditioner on the $\boldsymbol{\varepsilon}$ channel yields satisfactory convergence for the nonlinear conjugate gradients algorithm [26].

3. Results

Strong electric fields at liquid interfaces typical of battery systems necessitate a theory for the nonlinear response of the liquid environment, such as the nonlinear polarizable

§ Note that we employ an electron-is-positive charge convention, so that $\rho_{\text{nuc}} < 0$ and the charge of the electron is +1 in atomic units.

|| This preconditioner is derived from an approximation to the Hessian of A_{diel} with respect to $\mu(\mathbf{r})$ and $\boldsymbol{\varepsilon}(\mathbf{r})$ in the bulk linear limit.

continuum model of section 2. Section 3.2 calibrates the undetermined parameters of this theory against experimental solvation energies of molecules. For these molecules, and for metallic surfaces in section 3.3, we find results comparable to linear PCM's. However, for surfaces of ionic solids in section 3.4, we find that inclusion of nonlinear effects are necessary in order to obtain qualitatively correct results.

3.1. Computational Details

We perform all calculations in this paper using the open source plane-wave density functional software JDFTx [25] at a plane wave cutoff of 30 E_h (1 $E_h \equiv 1$ hartree ≈ 27.21 eV). These calculations employ norm-conserving pseudopotentials generated by the Opium pseudopotential generator [31] with the PBE exchange and correlation functional [32]. The pseudopotentials for metal atoms include partial core corrections [29], which are necessary to keep the fluid out of the pseudopotential cores as described in Section 2.7.

The choice of exchange-correlation functional for molecular and surface systems is not straightforward [33], and some argue that semi-local approximations can be inadequate for these systems [34]. Hybrid functionals which include exact exchange, or quantum Monte Carlo methods, are likely to be more accurate but are significantly more expensive than semi-local methods and hence unsuitable for rapid screening calculations. Here, we use the semi-local revTPSS exchange-correlation functional [35] which shows considerable promise for accurate calculations of surface phenomena including surface formation energies and molecular adsorption energies [36].

Molecular geometries for the calculations of section 3.2 are from the Computational Chemistry Comparison and Benchmark Database [37]. The surface geometries employed in sections 3.4 and 3.3 are constrained to the optimized bulk geometry for the central layer, while the remaining layers are fully relaxed for both the vacuum and fluid calculations. The fluid models assume ambient temperature $T = 298$ K for all calculations.

3.2. Calibration to molecular solvation energies

The nonlinear dielectric response of section 2.3 is completely constrained by *ab initio* and experimentally determined parameters, listed in table 3 for the solvents studied in this paper. However, the cavity shape function and the cavitation and dispersion terms, which are integral features of any polarizable continuum model, are unknown microscopic quantities that are typically constrained by a fit to solvation energies. Here, we fit the set of unknown cavity parameters for the nonlinear model and its linear limit to the same molecular solvation dataset using the same procedure, in order to facilitate a fair comparison between linear polarizable continuum models and our nonlinear theory.

The molecular solvation dataset must contain experimental data that is both reliable and readily available. Organic molecules solvated in water satisfy this criterion and are commonly used in fitting parameters for polarizable continuum models [10, 7]. The molecules used in our fit are listed in figure 3, and the known solvent parameters for water are listed in table 3. Of the remaining parameters, we set the shape function width parameter $\sigma = 0.6$ as in [6, 8] since the solvation energies are somewhat insensitive to it. We then determine the cavity transition electron density n_c and the effective cavity tension τ by a nonlinear least squares fit to the molecular solvation

	$n_c (a_0^{-3})$	$\tau (E_h/a_0^2)$	RMS Error (kcal/mol)
Nonlinear PCM	1.0×10^{-3}	9.5×10^{-6}	0.95
Linear PCM	3.7×10^{-4}	5.4×10^{-6}	1.05

Table 1. Fitted parameters of the nonlinear and linear polarizable continuum models (PCM) and the corresponding RMS errors for solvation energies of the molecules listed in figure 3.

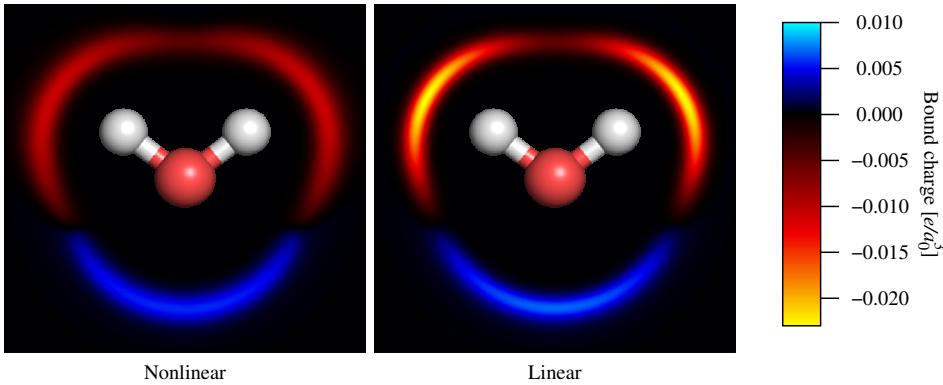


Figure 2. Bound charge in solvent water around a water molecule in the nonlinear and linear models. The smaller hydrogen atoms produce stronger fields on the solvent compared to the oxygen, resulting in much stronger saturation effects in the negative bound charge surrounding the hydrogens. In spite of the increased bound charge, the linear model yields approximately the same solvation energy as the nonlinear one due to compensation by the increased cavity size.

energy dataset.

The resulting fit parameters and optimized RMS error in solvation energy for the nonlinear and linear versions of the model are summarized in table 1. The smaller n_c , and hence larger cavities, for the linear model as compared to the nonlinear one offset the overestimation of electrostatic interactions due to the lack of saturation effects. The lowered cavity tension τ in the linear model then compensates for the increase in cavity area. Figure 2 demonstrates the consequences of these differences in the solvent bound charge surrounding a water molecule. The solvation energies predicted by the two models are in agreement as seen in figure 3, in spite of significantly larger bound charges in the linear case. Due to this cancellation, the linear model yields comparable accuracy to the nonlinear one for the solvation of organic molecules in water, but this is no longer the case when stronger electric fields come into play, as in some of the electrochemical systems we study next.

3.3. Solvation of metallic surfaces

Unlike the typical electrochemical interface, noble metal electrodes in electrolyte are less prone to complex chemical interactions at the surface, making them suitable candidates for an initial evaluation of our theory. Reactions are highly sensitive to the absolute electron chemical potential, which in experiments is typically reported relative to the standard hydrogen electrode (SHE). The absolute potential of the SHE relative to vacuum is difficult to establish experimentally; the estimates from different

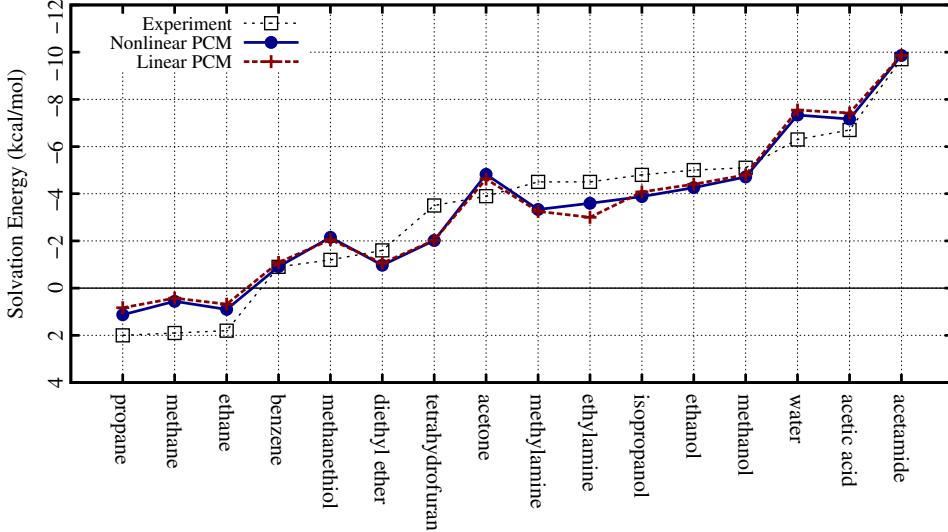


Figure 3. Solvation energies of molecules in water predicted by the nonlinear and linear polarizable continuum models compared against the experimental values from [38, 39].

	V_{SHE} (V)	V_{dip} (V)	RMS Error (V)
Nonlinear PCM	4.62	0.46	0.09
Linear PCM	4.68	0.40	0.09

Table 2. Offset between theoretical and experimental PZC's, V_{SHE} , determined by a fit using the systems of figure 4(a), with corresponding RMS errors. V_{SHE} represents the potential difference between an electron solvated deep in the fluid and the Standard Hydrogen Electrode. V_{dip} represents the potential due to the dipole moment at the fluid-metal interface, and is obtained as the difference between the theoretical PZC and the work function, averaged over the systems considered for each fluid model.

experimental methods range from 4.4 V to 4.9 V [40]. To make direct contact with experimental electrochemical observables, this experimentally uncertain quantity can be calibrated [8] in density-functional theory by comparing the theoretical chemical potentials for solvated neutral metal surfaces against the experimental potentials of zero charge (PZC's). The calibrations of the reference electrode potential within the linear and nonlinear models are remarkably similar, as shown in figure 4(a) and table 2.

The absolute potential of zero charge includes contributions from the work function, which is essentially independent of the fluid theory, and from the dipole moment in the interfacial layers of the liquid. The minor differences in the calibrations of the two theories stem from this dipole moment contribution, as shown for aqueous electrolytes in table 2. The variation of surface charge with electrode potential is also similar for the two models, as shown for the solvated Pt(111) surface of figure 4(b). In particular, the derivative of that variation, the so-called ‘double-layer’ capacitance, at the potential of zero charge is 14 and 15 $\mu\text{F}/\text{cm}^2$ for linear and nonlinear PCM

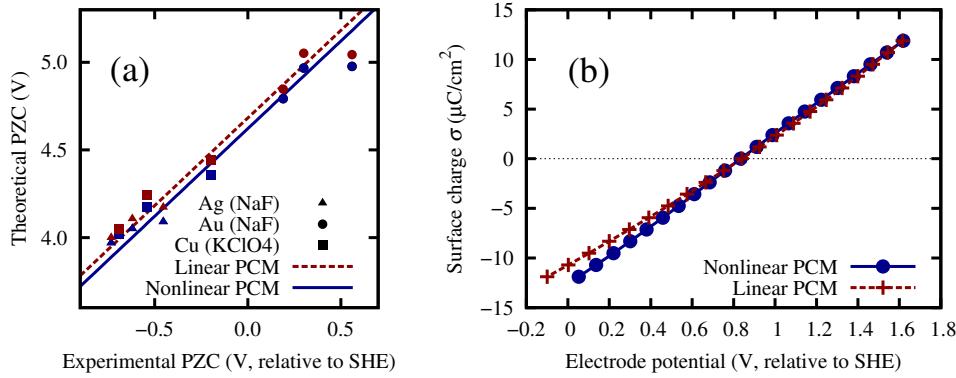


Figure 4. (a) Potentials of zero charge (PZC's) for the (111), (100) and (110) (left to right) each for silver (circles), gold (triangles), and copper (squares), predicted by the nonlinear and linear theories, compared to experiment [40]. The diagonal line for each theory compares theoretical and experimental values up to an overall fitted offset. (See table 2.) The silver and gold are solvated in aqueous 1 M NaF electrolyte (ionic radii Na: 1.16 Å F: 1.19 Å), while the copper is in aqueous 1 M KClO₄ electrolyte (ionic radii K: 1.52 Å and ClO₄: 2.26 Å). (b) Charge on a Pt(111) surface in 1 M aqueous KClO₄ as a function of potential relative to the standard hydrogen electrode (SHE) for the two theories.

respectively, which agrees well with an experimental estimate of $20 \mu\text{F}/\text{cm}^2$ [41] for the above system.

The agreement in the results of the linear and nonlinear theories demonstrated in figures 4(a,b) and table 2 is due to the same cancellation of errors at play for solvation of molecules. The linear theory misses saturation in the rotational dielectric response, thereby overestimating it, yet compensates with an increase in cavity size. This cancellation of errors is possible since the typical magnitudes of electric fields under typical operating potentials are similar to those of the molecular case, as shown in figure 7.

Both models predict an approximately linear variation of surface charge with electrode potential (figure 4(b)), which corresponds to a constant capacitance. This prediction contrasts with the experimental observation of a capacitance minimum at the potential of zero charge [41] due to ion adsorption on the electrode surface. The formation of this so-called inner Helmholtz layer between the solid surface and the solvent is precluded by the cavity ansatz of polarizable continuum models. These details require either a higher level of theory capable of describing layering effects of ions such as a classical density-functional approach, or the inclusion of explicit ions into the quantum mechanical calculation. Nonetheless, both the linear and nonlinear PCM adequately describe the basic features of the ideal electrochemical interface, and are suitable for describing chemical reactions at metal electrode surfaces as long as all chemical bonds are treated quantum-mechanically.

3.4. Solvation of ionic surfaces

The surfaces of electrodes typically contain ionic compounds whose structure and composition vary with the chosen electrolyte and operating conditions. The details of this interface play a critical role in battery performance, and an accurate description

Solvent	ϵ_b	ϵ_∞	p_{vac} (ea_0)	p_{mol} (ea_0)	N_{mol} (a_0^{-3})	τ (E_h/a_0^2)
Water	78.4	1.78	0.73	0.94	4.938×10^{-3}	9.5×10^{-6}
DMC	3.1	1.87	0.16	0.16	1.059×10^{-3}	2.05×10^{-5}
THF	7.6	1.98	0.69	0.90	1.100×10^{-3}	1.78×10^{-5}
DMF	38.0	2.05	1.50	2.19	1.153×10^{-3}	2.26×10^{-5}
PC	64.0	2.02	1.97	2.95	1.039×10^{-3}	2.88×10^{-5}
EC	90.5	2.00	1.93	2.88	1.339×10^{-3}	3.51×10^{-5}

Table 3. Parameters describing water and commonly used lithium battery solvents, Dimethyl Carbonate (DMC), Tetrahydrofuran (THF), Dimethylformamide (DMF), Propylene Carbonate (PC) and Ethylene Carbonate (EC). The vacuum dipoles (p_{vac}) and self-consistent solvated dipoles p_{mol} are computed using density-functional theory as described in section 2.3. All remaining parameters are constrained by measured bulk properties [44].

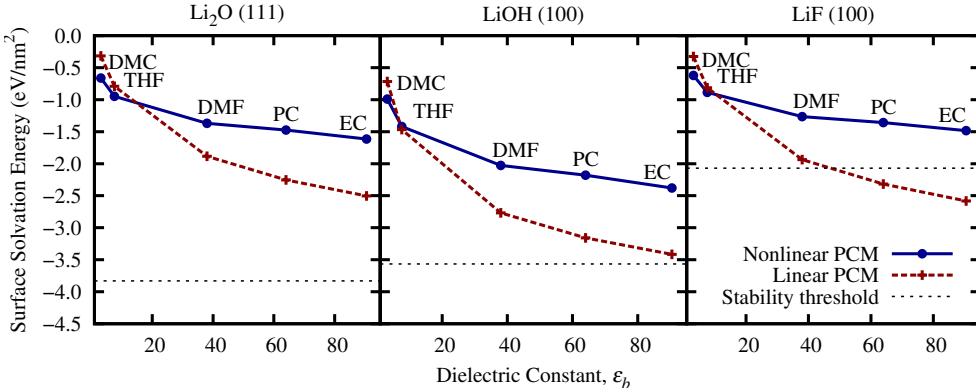


Figure 5. Solvation energies predicted by the nonlinear and linear models for surfaces of Li_2O , LiOH and LiF in the organic solvents from table 3. With increasing dielectric constant, the predictions of the linear model diverge from those of the nonlinear model due to missing saturation effects. This leads to qualitative differences here, unlike the case of the solvated molecules of figure 3. For some surfaces, the linear model suggests, perhaps incorrectly, that the flat surface is unstable by lowering the solvated surface energy relative to the bulk solid.

of such surfaces in electrolyte environments is therefore crucial for modeling efforts towards improving battery systems. Reactions at the surface of a lithium metal anode, for example, can form Li_2O , LiOH and LiF at the solid electrolyte interface [42, 43]. Here, we study these surfaces in contact with different organic solvents typical of battery systems as a testbed for fluid models applicable to battery systems.

The solvents selected for this study are listed in table 3. Due to the dearth of experimental data for corresponding solvation energies, we here use the cavity shape parameters determined by the fit in section 3.2. We replace the effective tension τ by the experimental surface tension, ignoring dispersion effects which are insignificant on the scale of the electrostatic energies in these highly polar systems. All remaining physical parameters that determine the dielectric response are constrained by experiment and *ab initio* calculations, as discussed in section 2.3.

The linear and nonlinear models predict similar solvation energies for the

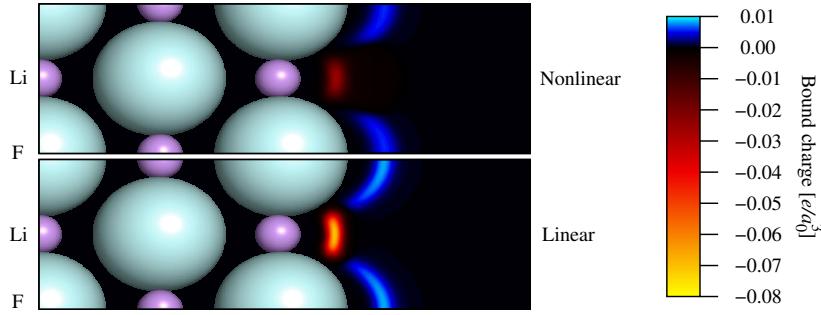


Figure 6. Bound charge in solvent Ethylene Carbonate (EC) around a LiF (100) surface in the nonlinear and linear models, shown in a (011) slice. Saturation effects are stronger next to the smaller Li⁺ cations which produce significantly stronger fields on the solvent compared to the larger F⁻ anions. In contrast to a water molecule solvated in water (Figure 2), these effects are strong enough to qualitatively alter solvation energies, as shown in figure 5.

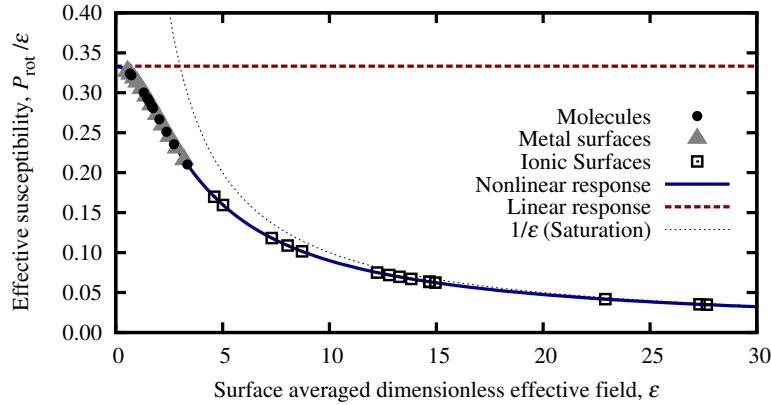


Figure 7. Effective rotational susceptibility at the average value of the dimensionless effective field ϵ at the cavity surface (solvent-solute interface) for solvated molecules (circles), charged metal surfaces (triangles) and ionic surfaces (squares). The reduction in susceptibility due to saturation effects captured by the nonlinear model is missed by the linear one. Unlike the case of molecules and metal surfaces, the order of magnitude overestimation of the susceptibility by the linear model for ionic surfaces is not compensated by the increase in cavity size.

aforementioned ionic compounds of lithium in solvents with low dielectric constants, as shown in figure 5. However, with increasing dielectric constant, the magnitude of the solvation energy increases more rapidly for the linear model, leading to disagreement by up to a factor of two for the most polar solvents. The linear model overestimates the electrostatic interaction due to a lack of saturation effects, but unlike in the molecular case, the increase in cavity size is insufficient to compensate for this error. In fact, for lithium fluoride in ethylene carbonate, as seen in figure 6, the linear model overestimates the bound charge by an order of magnitude. Indeed, in this case, the result is a qualitative difference in the predicted stability of the solvated surface relative to the solid, with the linear model even predicting the solid to be thermodynamically unstable with respect to the formation of surfaces in this system.

The qualitative inadequacy of the linear model for ionic surfaces derives from the significantly stronger electric fields in these systems compared to solvated molecules and metallic surfaces. Figure 7 compares the average electric field and the corresponding rotational susceptibility at the solute-solvent interface for all the systems discussed above. The least polar neutral ionic surface still imposes a higher electric field than the most polar molecule or charged metallic surface at chemically relevant electrode potentials. The order of magnitude reduction in rotational susceptibility due to saturation effects in the ionic surfaces, compared to the modest reduction for the other systems, necessitates a nonlinear theory for the study of these types of battery systems.

4. Conclusions

Ab initio studies provide key insights into chemical processes in a wide range of systems, but have not yet approached battery chemistry with a realistic description of the electrolyte environment. Continuum solvation models provide an intuitive and computationally-efficient description of the environment and enable a focused study of the complex subsystems that require treatment at the electronic structure level. Our results indicate that standard polarizable continuum models fit to molecular solvation data perform poorly when applied to polar surfaces of the type often encountered at the SEI in battery systems. Consequently, one must exercise caution when attempting to apply standard solvation models available in both quantum chemical [7, 45, 46] and condensed matter [10, 47] *ab initio* software packages. As an alternative, the nonlinear theory presented here and implemented in [25] leverages the computational simplicity of the standard polarizable continuum models and extends their applicability to systems with the strong electric fields associated with ionic surfaces in electrochemical systems.

The importance of nonlinear solvent response depends on the strength of electric fields at the interface, which in turn varies dramatically with system type, as highlighted in figure 7. For systems with moderate field strengths, such as the molecules and metal surfaces studied here, the linear models can compensate for the overestimated electrostatic response through an increase in cavity size. However, for systems with higher field strengths, such as ionic surfaces, this compensation is insufficient. The nonlinear polarizable continuum model developed here consistently describes all of these systems, and along with the technique developed in section 2.6 to determine the absolute electron chemical potential, enables electronic structure predictions for real electrochemical systems as a function of electrode potential.

This theory provides a cost-effective yet accurate method for calculating properties of electrochemical systems of technological relevance, such as high-throughput screening potential battery materials. Cleaner surface experiments analogous to the solvation datasets available for molecules will help further refine the theory of solvation for these systems. In our study of battery electrode materials, we showcase our theory with electronic density functional calculations. The method can easily be used with other electronic theories such as coupled cluster or quantum Monte Carlo [14], enabling the study of non-equilibrium properties. Using these techniques, we can include nonlinear solvation in transition state calculations important for understanding processes in energy systems, such as catalysis in fuel cells and ion diffusion on battery electrodes.

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